RECENT DEVELOPMENTS IN TWO-STAGE COAL LIQUEFACTION AT WILSONVILLE,

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INTRODUCTION

This paper will present results from the Advanced Coal Lique-
faction R&D Facility at Wilsonville, Alabama. The primary
sponsors are the U.S. Department of Energy (DOE) and the Electric
Power Research Institute (EPRI). Amoco Corporation became a
sponsor in 1984 through an agreement with EPRI. The facility is
operated by Catalytic, Inc., under the management of Southern
Company Services, Inc.

RUN 247

Run 247 employed Illinois No. 6 coal in a configuration called
the Reconfigured Integrated Two-Stage Liquefaction (RITSL) mode
(Figure 1). Coal is slurried with a recycled process solvent and
fed to the dissolver under hydrogen pressure where thermal
liquefaction takes place. Thermal distillate is separated by
fractionation, and the vacuum bottoms along with a heavy fraction
of distillate make up the feed to the hydrotreater. This
hydrotreater feed containing the thermal resid, unconverted coal,
and ash is fed directly to the ebullated bed hydrotreater. The
vacuum-flashed bottoms from the hydrotreater is the feed to the
Critical Solvent Deashing (CSD) unit. The recycle solvent is
composed of the deashed hydrotreater resid (HR) and hydrotreated
distillate solvent.

Prior to Run 247, most runs had used the Integrated Two-Stage
Liquefaction (ITSL) configuration, as illustrated in Figure 2. In
the ITSL mode, the vacuum resid from the thermal liquefaction
stage is deashed in the CSD unit before being fed to the hydro-
treater.

Operation in the RITSL configuration was a step in the program to
operate with close-coupled reactors, where the products from the
liquefaction stage would be fed directly to the hydrotreater
without any intermediate ash or distillate separation.

Because the hydrotreater feed was not deashed, it contained all
the coal ash along with unconverted coal and heavy organics that
would normally be removed in the deashing step. Thus, there was
concern that the catalyst deactivation rate would increase.
Another operability question concerned the effect of the RITSL
mode on deashing. Since the feed to the CSD unit would be the
vacuum-flashed bottoms from the hydrotreater, the CSD feed
properties were expected to be different from feed properties
that had previously been experienced.

Run 247 Results

The hydrotreater catalyst performed well in the RITSL mode. The
catalyst used for all the runs in this report was Shell 324-M, a
unimodal Ni-Mo catalyst. Throughout the run, catalyst activity
measured by resid conversion was higher than in previous runs in

the ITSL configuration. This catalyst was aged to 1225 lbs (resid + UC + ash)/lb catalyst. The nondeashed feed did not cause serious deactivation of the catalyst (1).

Operability of the CSD unit with hydrotreated feed was satisfactory. The CSD feed did have different properties than feeds in the ITSL mode, but process adjustments were made which provided good deashing performance.

Representative Run 247 results in the RITSL mode are compared to a previous ITSL run in Table 1. The second column (243JK/244B) lists ITSL data that compare closely in operating conditions and cover a similar range of batch catalyst age as the RITSL data (247D). The RITSL distillate yield was 62%, compared to 59%. However, the distillate yields combined with the resid yields indicate that both configurations would have total liquid yields of 65% with zero resid.

A major difference is that the hydrogen consumption was 1% higher with RITSL, so the hydrogen efficiency was lower. The higher hydrogen consumption with RITSL is thought to be primarily related to higher resid reactivity. This improved hydrogenation activity is apparently caused by differences in the feed hydrocarbons or the presence of coal ash particles or both.

Run 247 Product Quality

Product blends were made by mixing product streams in the proportions of their production rates. These blends were then fractionated into boiling point cuts and elemental analyses were made of the individual fractions. Table 2 shows the product analyses for a Run 247 sample compared to a Run 244 sample to enable a direct comparison of products produced in the RITSL and ITSL configurations. The hydrogen contents of comparable fractions is higher, by 0.8-1.2%, for RITSL. The H/C ratios are higher by 0.10-0.16. In general, the RITSL product had lower levels of nitrogen and sulfur. These results appear to be evidence of increased hydrogenation. Therefore, the higher hydrogen consumption seems to be a trade off with improved product quality.

Mixing Study

A mixing study was conducted to quantify the degree of mixing in the dissolver. Mixing was studied by using radioactive tracer tests. The residence time distributions were fitted by a simple model. Importantly, the dissolver was found to be well mixed (3).

RUN 248

The configuration used at the beginning of Run 248 was the Double-Integrated Two-Stage Liquefaction (DITSL) mode, which is shown in Figure 3. This differs from the ITSL mode in that only the Light Thermal Resid (LTR) is routed through the hydrotreater. The heavier Thermal Resid (TR) is recycled directly to the thermal first stage. A potential advantage of the DITSL configuration is that a smaller hydrotreater might be possible because only the LTR stream is hydrotreated (2).

In the DITSL configuration, the heavy thermal resid is recycled to the liquefaction stage without going through the hydrotreater. Thus, the TR must be converted in the thermal stage for the DITSL mode to be viable. Iron oxide was used to promote resid conversion (4). Dimethyl Disulfide (DMDS) was added to the coal slurry to provide a source of hydrogen sulfide to convert the iron oxide to pyrrhotite as the slurry flowed through the preheater. This was the same method that was used successfully in Run 246 (2).

Before beginning the run, the 12-inch diameter dissolver was replaced by a 5.2-inch diameter Low Contact Time (LCT) dissolver. This was done to allow operation at lower liquefaction reactor volumes than could be achieved with the 12-inch dissolver. The intent was to investigate reaction times somewhat longer than had been used in the Short Contact Time (SCT) tests in Run 242 (5).

Run 248 Results

Operation in the DITSL configuration was difficult. The major operability problem was high viscosities of the TR, the process solvent, and the coal slurry. The recycle of the heavy TR directly from the CSD unit resulted in a buildup of preasphaltenes, which caused the high viscosities. Process variable adjustments were made in an attempt to achieve viable operations in the DITSL mode. The dissolver outlet temperature was raised to 840°F to increase the severity for resid conversion. However, resid conversion in the thermal unit was not sufficient to allow satisfactory operation in the DITSL configuration.

Satisfactory operability was obtained by changing to the ITSL configuration. The distillate yield was 64% and the resid make was 3%, for a total liquid yield of 67% (248D). This compares favorably to the 65% yields shown earlier for the RITSL and ITSL configurations with Illinois No. 6 coal. Because of other process variable differences, most notably dissolver temperature, it can not be concluded from these results if iron oxide caused an improvement in distillate yield.

The addition of iron oxide and DMDS was stopped, to begin a series of tests at different reactor volumes. After a three-day test at 100% LCT without iron oxide, the dissolver volume was reduced successively to 50% and then to 25% LCT dissolver volume. Coal conversions with volumes of 100%, 50%, and 25% were 92%, 90%, and 88% MAF coal, respectively. As expected for the reduced contact times, resid makes increased and distillate makes and hydrogen consumptions decreased.

Conditions and two-stage liquefaction (TSL) yields for the 50% LCT period (248F) are compared to Run 242 SCT results in Table 1. Coal space velocities using the reaction volume above 700°F were comparable for these two conditions. The yields were very similar, though SCT showed an advantage in lower gas make and hydrogen consumption. A close examination of conditins indicated that the average reaction temperature was higher for 248F.

Run 248 Product Quality

Properties of a fractionated product blend from period 248D (ITSL with iron oxide) are shown in Table 3. As can be seen, the product boiling below 650°F is 67% of the total blend, which is comparable to that obtained in Run 244 without iron oxide (Table 2).

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The naphtha from 248D had higher hydrogen content (13.76 vs 12.86) but the nitrogen and sulfur were higher. The analyses for the distillate and gas oil fractions were similar, with 248D showing slightly higher nitrogen and sulfur contents. The API gravities showed that the naphtha and distillate for 248D were heavier than those from Run 244.

RUN 249

A major objective was to obtain process yield data using subbituminous coal with a well-mixed dissolver. A pumparound loop was installed to provide back mixing of the 12-inch dissolver.

The RITSL configuration was used to provide a data base for predicting process performance with subbituminous coal in a close-coupled configuration.

Two additives were investigated for enhancement of conversion of the subbituminous coal. The effectiveness of iron oxide with DMDS had been demonstrated earlier (2). Work at the University of Wyoming had shown some very interesting results related to coal drying and the use of water in liquefaction of subbituminous coal (6). Coal conversions were improved when coal was not completely dried or even when water was added back to a coal slurry of dried coal before liquefaction. The water effect was found to be additive to the iron oxide effect on coal conversion. The effect of water addition was tested by adding water at the rate of 15% MF coal to the coal feed slurry.

Run 249 Results

The run was started with the dissolver at 790°F and the hydrotreater at 670°F and with no iron oxide or water addition. The coal conversion was 82%. Coal conversion was increased to 90% by adding iron oxide plus DMDS and by increasing the dissolver temperature from 790 to 810°F. Water addition increased coal conversion by 3%. Iron oxide and DMDS addition were discontinued to test whether water addition without iron oxide could maintain coal conversion. Coal conversion decreased significantly, from 92 to 84%. Thus, water addback did not enhance coal conversion enough to enable operation without the iron oxide.

For the 1.5% iron oxide addition rate, the coal sulfur content was calculated to be sufficient to convert the iron oxide to pyrrhotite. This was tested by stopping the DMDS addition and no reduction in coal conversion was observed. Therefore, iron oxide was used without the addition of DMDS for the last two months of the run.

Energy rejection was high throughout this run because the CSD feed was very soluble and the solubility changed with various operating variable adjustments. Energy rejection was reduced by changing solvent type and adjusting operating conditions. The CSD experience gained in this run will be valuable in processing the highly soluble feeds that are expected to be encountered in the close-coupled operations.

Selected process conditions and yields for Run 249 are shown in Table 1. The only difference in periods 249D and 249E is that water addback was used in 249D.

The negative resid make for 249E indicates that more resid was being converted than was being made, so that resid was being consumed from inventory. The C_4+ distillate yield for 249E would be about 53% if the resid make had been zero. Thus, there was practically no effect of water addback on distillate yield for this comparison.

The last major period of the run, designated 249H, was an ash recycle test. The purpose of this test was to remove ash from the system by using a purge of hydrotreater vacuum bottoms instead of using the CSD unit. The ash content of the purge stream was increased by recycling a portion of the hydrotreater atmospheric flashed bottoms to the dissolver. This recycled solvent contained ash, iron oxide, unconverted coal and hydro-treated resid and distillate. By using this method, the solids content of the vacuum bottoms purge stream was increased to about 50% unconverted coal and ash. The ash content was 32%.

The recycle test resulted in significantly increased coal conversion. The 94% coal conversion obtained in period 249H is the highest obtained with subbituminous coal at Wilsonville. It is notable that this high conversion was obtained with a moderate dissolver temperature of 802°F. The increased coal conversion was probably due to additional conversion of the unconverted coal in the recycle stream. The recycled ash and iron oxide also probably contributed to enhanced reactivity.

The yield results are similar to 249E, but the hydrogen con-sumption was higher. These results were encouraging and suggest that a vacuum tower could be used as an alternate method of removing ash from the system.

A comparison of data for 249E and 2496G in Table 1 provides a comparison of the RITSL and ITSL results with subbituminous coal. A number of differences are apparent in the operating condi-tions. In particular, Run 249E had a lower dissolver temperature and a considerably higher hydrotreater temperature. Also, 249E had a forced back-mixed dissolver while 246G did not. Surpri-singly, the yields are fairly similar. As a result of the lower dissolver temperature, 249E had a lower gas make. The sum of distillate and resid is comparable for the two periods. Several factors may have contributed to the higher hydrogen consumption of 249E, but the RITSL configuration is probably the main reason.

An analysis of catalyst behavior in Run 249 has not been com-pleted. However, the catalyst performed adequately throughout the run and a catalyst age of 1870 lb (resid + UC + ash)/lb was reached. The catalyst used for Run 249 was the Shell 324-M catalyst used in Run 246, with an initial age of 617. Catalyst deactivation was observed during the run, but the resid con-version activity appeared to be relatively constant over the last half of the run.

1985 ACCOMPLISHMENTS

The RITSL configuration was demonstrated for both bituminous and subbituminous coals and the results were positive. These runs provide a solid basis for close coupling the reactors. A very successful mixing study was performed to quantify the degree of

mixing in the thermal reactor. Iron oxide and water were tested
as disposable catalysts. Iron oxide has been tested in both the
ITSL and DITSL configurations with both coals. The experience
with increased CSD feed solubility broadened the knowledge of CSD
operations. This will be applicable in the close-coupled runs.
Lastly, an alternate method of removing ash from the system was
demonstrated in the ash recycle test. This provides additional
flexibility for future runs.

FUTURE WORK

The emphasis is on experimentation with close-coupled reactors.
The Wilsonville plant has been modified by the addition of a
reactor vessel adjacent to the hydrotreater to operate in a
close-coupled fashion. The initial run will be a thermal-
catalytic run, but the equipment is capable of operating with
ebullated catalyst beds in both reactors. There are plans to
test alternate catalysts.

The coal liquefaction data base will be expanded by parametric
studies and by increasing efforts in the area of process modeling
and simulation.

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TABLE 1

PROCESS CONDITIONS AND YIELDS

	247D	243JK/244B	248D	248F	242BC	249D	249E	249H	249G
Run No.									
Configuration	RITSL	ITSL	ITSL	ITSL	ITSL-SCT	RITSL	RITSL	RITSL	ITSL
Coal	Ill. 6	Ill. 6	Ill. 6	Ill. 6	Ill. 6	Ill. 6	Wyo.	Wyo.	Wyo.
Thermal Stage									
Temperature (°F)	810	810	834	835	860*	796	796	802	813
Coal Space velocity (lb/hr-ft^3(>700°F))	27	28	31[1]	44[1]	43	14	14	14	17
Solvent-to-Coal Ratio	1.8	1.8	1.8	1.8	1.8	1.5	1.5	2.0	1.8
Solvent Resid Content (wt %)	44	50	45	45	46	30	29	22	30
Iron Oxide (% of MF Coal)	0	0	2.0	0	0	1.5	1.5	1.5	2.0
DMDS Addition	0	0	Yes[2]	0	0	0	0	0	Yes[2]
Catalytic Stage									
Temperature (°F)	710	720	705	728	720	700	700	700	625
Space Velocity (lb feed/hr/lb cat)	0.9	1.0	0.7	0.7	1.0	1.3	1.2	1.6	1.0
Feed Resid Content (wt %)	51	55	57	57	55	35	34	27	34
Catalyst Age (lb resid/lb cat)	445-670[3]	350-850	260-287	359-396	278-441	1119-1183[3]	1208-1246[3]	1683-1703[3]	496
Yield (% MAF Coal)[4]									
C$_1$-C$_3$ Gas (Total Gas)	6(12)	6(12)	8(13)	7(12)	4(9)	7(18)	6(14)	7(16)	9(19)
Water	9	9	8	9	10	14	14	14	11
C$_4^+$ Distillate	62	59	64	54	54	53	57	56	53
Resid	3	6	3	8	8	1	-4	-4	1
(Total Liquid Product)	(65)	(65)	(67)	(62)	(62)	(54)	(53)	(52)	(54)
Hydrogen Consumption	-6.1	-5.1	-5.6	-5.3	-4.9	-5.7	-5.8	-6.3	-5.4
Hydrogen Efficiency (lb C$_4^+$ Dist/ lb H$_2$ Consumed)	10.2	11.5	11.3	10.2	11.0	9.3	9.9	8.9	9.8
Energy Rejected to Ash Conc. (%)	22	22	19	23	25	21	24	26	21

Inlet hydrogen partial pressure 2040 psi
*preheater outlet temperature. Dissolver was bypassed in Short Contact Time Run 242.
[1]Used LCT 5.2-inch diameter dissolver. Other runs used 12-inch diameter dissolver.
[2]Dimethyl Disulfide added at 1.1 x stoichiometric amount to convert Fe$_2$O$_3$ to FeS.
[3]Catalyst age for RITSL is lb(resid + ash + unconverted coal)/lb catalyst.
[4]Elementally balanced yield structures.

TABLE 2

properties of distillate product

sample: Wilsonville synthetic crude blend representative of TSL product slate

distillation cut	wt% of sample	elemental (wt%)					API gravity (60/60)
		C	H	N	S	O (diff)	
(A) run 244 (catalyst age ∿ 1600 lbs resid/lb cat, HTR temp ∿ 730°F)* ITSL configuration							
naphtha (IBP-360°F)	18.4	85.21	12.86	845ppm	0.36	1.50	43.1
distillate (360°F-650°F)	45.7	86.34	10.73	0.23	0.22	2.48	18.6
gas oil (650°F-1000°F)	35.0	89.07	9.69	0.31	0.16	0.76	7.3
resid (1000°F+)	0.9	86.71	6.94	1.13	0.60	3.15	—
(B) run 247 (catalyst age ∿ 283-372 (lbs resid + UC + ash)/lb cat, HTR temp ∿ 700°F) RITSL configuration (247C-II)							
naphtha (IBP-360°F)	14.9	85.50	14.07	500ppm	0.35	0.03	—
distillate (360°F-650°F)	49.8	86.74	11.54	0.23	0.16	1.33	—
gas oil (650°F +)	35.3	89.48	10.44	0.06	0.02	0.00	—

*work performed by Amoco Oil Company

TABLE 3

properties of distillate product

sample: Wilsonville synthetic crude blend representative of TSL product slate

distillation cut	wt% of sample	elemental (wt%)					API gravity (60/60)
		C	H	N	S	O (diff)	
(A) run 248 (catalyst age ∿ 300 lbs resid/lb cat, HTR temp ∿ 700°F) ITSL configuration (248D)							
naphtha (IBP-350°F)	18.6	84.63	13.76	0.13	0.65	0.83	42.4
distillate (350°F-650°F)	48.1	84.45	10.94	0.23	0.37	4.01	13.2
gas oil (650°F+)	33.3	89.11	9.41	0.43	0.18	0.87	0.3
total blend	100.0	85.72	10.76	0.22	0.42	2.86	14.1

two-stage liquefaction
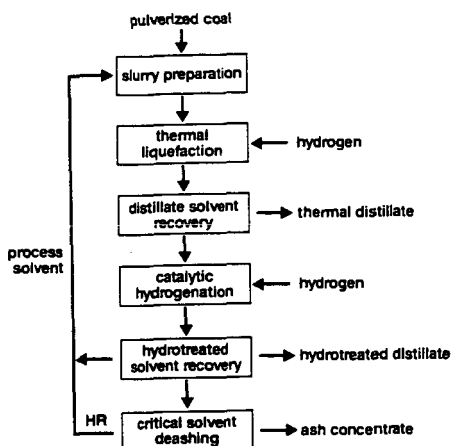## reconfigured mode (RITSL)

FIGURE 1

two-stage liquefaction
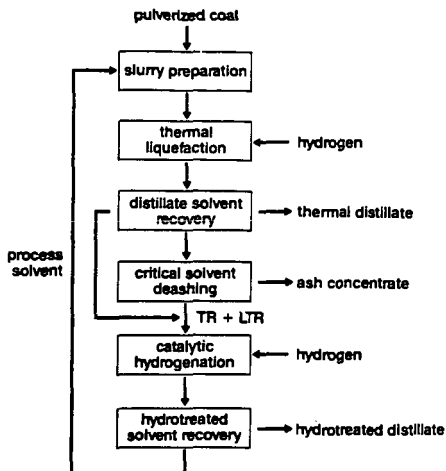## integrated mode (ITSL)

FIGURE 2

two-stage liquefaction
double-integrated mode (DITSL)

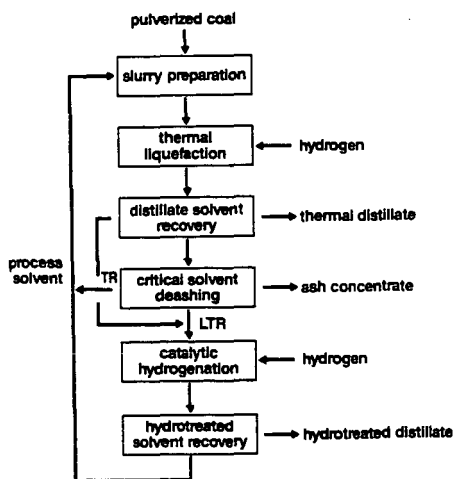

FIGURE 3